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Synthesis of novel bithiophene derivatives with an organosilanylene bridge, and their applications to electron-transporting materials in EL devices

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Abstract

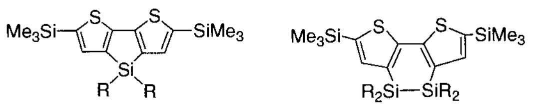
Compounds having two bithiophene units linked by an organosilicon bridge were prepared. Their UV spectra and cyclic voltammograms indicated that the compounds have the low-lying LUMO. The electron transporting properties of the present silicon-bridged bithiophene derivatives were evaluated by the performance of electroluminescent (EL) devices having vapor deposited silicon-bridged bithiophenes, Alq, and TPD layers, as the electron-transport, emitter and hole-transport, respectively. By applying the bias voltage on the devices, the devices emitted green EL originated from the Alq emission with the maximum luminance of 8500 cd m^{-2}. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Silole; Electron-transport; EL device

1. Introduction

There has been current interest in the chemistry of silole (silacyclopentadiene) ring systems [1]. The high electron affinity of silole derivatives arising from the low-lying LUMO energy level provides the chance to use them as the functionality materials, such as organic semiconductors [2] and electron transport in the electroluminescent (EL) devices [3]. Recently, it has been also reported that the vapor deposited films of silole derivatives and spin-coated films of polymers having 1,1-silole-diyl units may be used for the single layer EL device system [4].

In our effort to develop novel silole-containing compounds [5], we have synthesized dithienosiloles and disilacyclohexadienes, in which a bithiophene system is intramolecularly bridged by an organomono- or disilanylene unit at the β,β′-positions (compounds **3a** and **4a** in Chart 1) [6]. Interestingly, introduction of the Si-bridge significantly affects the electronic states of the bithiophene derivatives and lowers the LUMO energy level, as being applicable to the electron transport in electroluminescent (EL) devices. In fact, the devices with the structure of ITO (indium tin oxide)/TPD (40 nm)/Alq (50 nm)/Si-bridged bithiophene (10–20 nm)/Mg–Ag, where TPD (*N*,*N*′-diphenyl-*N*,*N*′-di(*m*-tolyl)-biphenyl-4,4′-diamine), Alq (tris(8-quinolinolato)-aluminum(III)), and Si-bridged bithiophene are the hole-transport, emitter and electron-transport, respectively, emit strong EL. Of these, the maximum



3a

R_2 = Ph_2, p-Tol_2, $Me(SiMe_3)$, $Ph(SiMe_3)$

4a

R_2 = Me_2, Et_2, PhMe

Chart 1.

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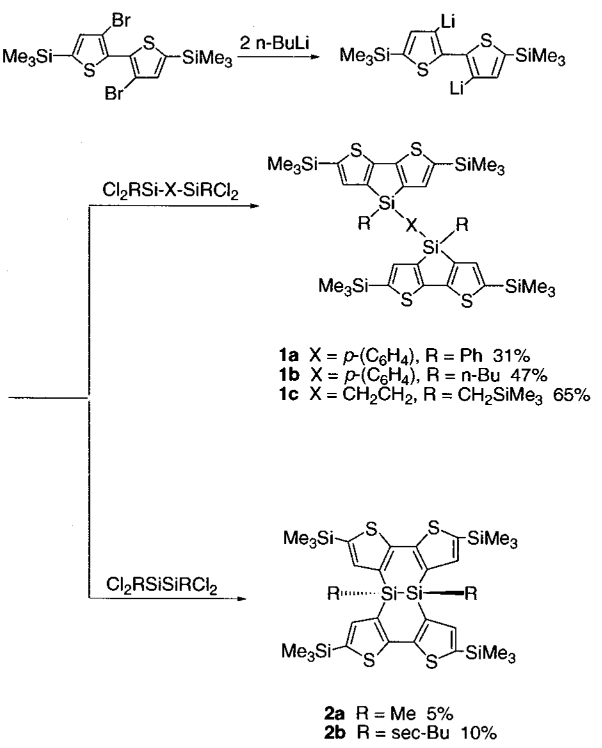

Scheme 1.

Table 1
Properties of dithienosilole and dithienodisilacyclohexadiene derivatives

Compound	Absorption [a] (λ_{max}, nm)	CV [b] Epa [c] (V)
1a	360	1.24
1b	355	1.18
1c	352	1.05
2a	348, 376 (sh)	1.10
2b	380	1.16
3a	350–358	1.08–1.25
4a	350–353	1.05–1.15

[a] In THF.

[b] In acetonitrile containing $LiClO_4$ as the supporting electrolyte using glassy carbon as the working electrode.

[c] Anodic peak potential vs SCE.

luminance of 8000 cd m^{-2} was achieved by the device having a 4,4-di(*p*-tolyl)-2,6-bis(trimethylsilyl)dithienosilole (**3a**, *R* = *p*-Tol) layer as the electron transport [7]. On the basis of the comparison of performance of the EL devices, we concluded that the electron-transporting properties of **3a** (*R* = *p*-Tol) are comparable or a little superior to those of Alq, which is known as a typical electron-transporting-emitting material.

To obtain Si-bridged bithiophenes with higher electron transporting properties, we synthesized novel bithiophene derivatives, in which two bithiophene systems are linked by an organosilanylene bridge, and investigated their properties with respect to the UV spectra and cyclic voltammograms (CVs). EL device performance using the present bithiophene derivatives as the electron-transport, was also studied.

2. Results and discussion

2.1. Synthesis of Si-bridged bithiophenes

The reactions of 3,3′-dilithio-5,5′-bis(trimethylsilyl)-2,2′-bithiophene with bis(dichlorosilyl)-compounds gave the corresponding bridged dithienosiloles (**1a**–**c**) in moderate yields as shown in Scheme 1. Similar reactions of tetrachlorodisilanes produced compounds with fused dithienodisilacyclohexadiene units (**2a**, **b**). In these reactions, no dithienosilole derivatives were obtained. The rather low yields of **2a**, **b** may be due to both the formations of unidentified byproducts in low yield and the decomposition of **2a**, **b** during work up. In fact, small amounts of protodetrimethylsilylation products were found to be formed by GC–MS analysis, when compounds **2a**, **b** were subjected to silica gel column chromatography.

Compounds **1a**–**c** and **2a**, **b** were obtained as the solids. M.p. of bridged dithienosiloles **1a**–**c** are around 130–150 °C, while disilacyclohexadiene derivatives **2a**, **b** melt at much higher temperature of ca. 270 °C. The structures of the **1a**–**c** and **2a**, **b** were verified by spectroscopic and elemental analysis. Furthermore, the crystal structure of **2b** was tentatively solved by an X-ray diffraction study [8]. The crystal quality was not good enough, and moreover, the thermal displacements of the atoms are too large, in particular for the *sec*-butyl groups attached to the silicon atoms, to discuss the detailed crystal structure of **2b**. However, it was undoubtedly indicated that the fused disilacyclohexadiene system must have the trans geometry with respect to the central Si–Si bond.

2.2. UV spectra and CVs of *1a–c* and *2a*, *b*

Table 1 summarizes the UV absorption maxima and oxidation peak potentials in the CVs of compounds **1a**–**c** and **2a**, **b**, together with those of simpler dithienosilole and disilacyclohexadiene derivatives, reported previously (**3a** and **4a** in Chart 1) [6b]. Compounds **1a**–**c** and **2a**, **b** underwent irreversible anodic oxidation in their CV experiments and we could not observe the cathodic counter peaks, as in the case of **3a** and **4a**. As can be seen in Table 1, the UV and CV data of **1a**–**c** closely resemble those of **3a**, indicating that bridging the dithienosilole units by the organic linkage affects little the electronic states of dithienosiloles and the two dithienosilole units are electronically rather isolated. The slight decrease in oxidation potential in the order of **1a** > **1b** > **1c** may be due to the introduc-

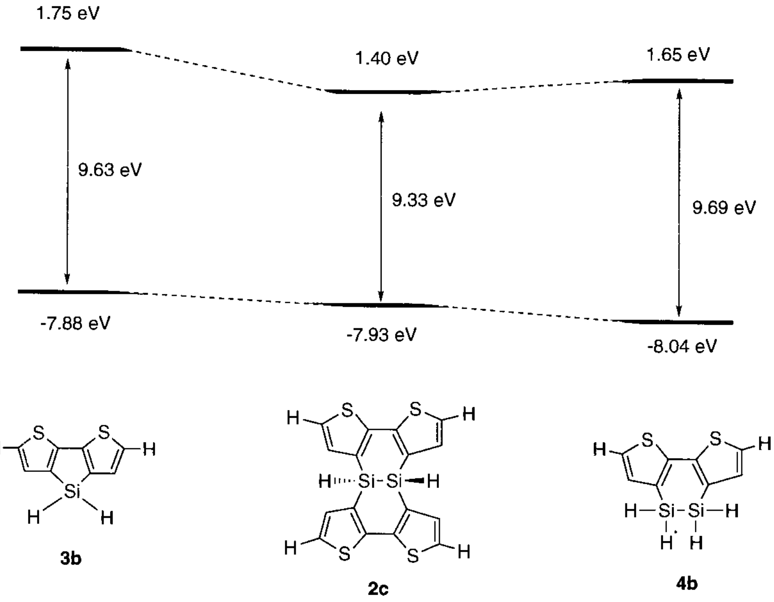

Fig. 1. Relative HOMO and LUMO energy levels for model compounds, derived from MO calculations at RHF/6-31G level.

tion of electron-donating alkyl groups on the silole silicon atom. The absorption maxima of **2a**, **b** appear at longer wave length than those of **4a**. Since the anodic peaks of **2a**, **b** are at almost the same energy as those of **4a**, the red shifts of absorption maxima of **2a**, **b** from **4a** seem to be due to the lower-lying LUMO of **2a**, **b** mainly. This is in good agreement with the results of the ab initio molecular orbital (MO) calculations on simplified model compounds (Fig. 1). The MO calculations at RHF/6-31G level [9] predicted that the HOMO–LUMO energy gap is smaller for **2c** than for **4b** by 0.36 eV. The difference in HOMO energy levels of **2c** and **4b** was calculated to be 0.11 eV, while that of LUMOs was predicted to be much larger (0.25 eV), being primarily responsible for the smaller HOMO–LUMO energy gap.

2.3. EL performance of the devices having Si-bridged bithiophenes as the electron-transport

To evaluate electron-transporting properties of the present Si-bridged bithiophenes, we fabricated triple-layer EL devices having a vapor-deposited layer of **1b** or **2b** as the electron-transport. The structure of the devices and the thickness of the layers were ITO/TPD (40 nm)/Alq (50 nm)/**1b** or **2b** (10–20 nm)/Mg–Ag (device 1 for **1b** and device 2 for **2b**). In these devices, TPD, **1b** or **2b**, and Alq layers were used as the hole- and electron-transport and emitter, respectively. ITO and Mg–Ag were the anode and cathode. Fig. 2 depicts the current density–voltage (I–V) characteristics of the devices 1 and 2, indicating that device 3 exhibited better I–V characteristics than device 1. Fig. 2 represents the luminance–voltage (L–V) characteristics of the devices. In the low-voltage region up to 16 V, device 2 emitted higher luminance than device 1, in accordance with the I–V characteristics. However, at higher voltage, the luminance of device 2 dropped probably due to the decomposition of the **2b** layer by melting or crystallization, while that of the device 1 increased up to 17 V to reach the maximum value of 8500 cd m^{-2} (Fig. 3).

The threshold voltages of 100 mA cm^{-2} and 1000 cd m^{-2}, and the maximum current densities and luminance of devices 1 and 2 are summarized in Table 2, in comparison with those of the device of the same structure having simpler dithienosilole **3a** ($R = p$-Tol) or **4a** (R_2 = Ph, Me), as the electron-transport, and also the data of the reference device of ITO/TPD (40 nm)/Alq (50 nm)/Mg–Ag having an Alq layer as the electron-transporting emitter [6b,7]. The electron-transporting properties of the vapor-deposited films estimated by the

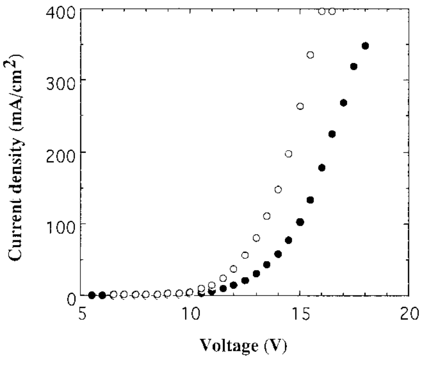

Fig. 2. Plots of operating voltage vs current density of (●) device 1 and (○) device 2.

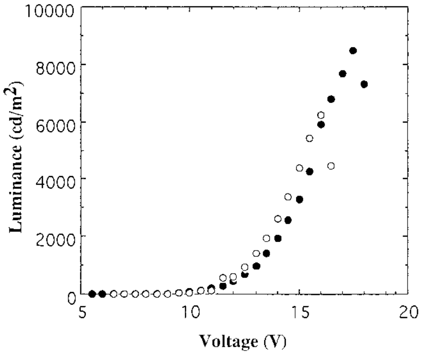

Fig. 3. Plots of operating voltage vs luminescence of (●) device 1 and (○) device 2.

I–V and *L–V* characteristics of the devices shown in Table 2, were improved in the order of **3a** ($R = p$-Tol) > Alq > **4a** ($R_2 =$ Ph, Me) > **2b** > **1b**, although the maximum luminance of the device 2 was a little higher than those of the devices with **3a** ($R = p$-Tol) and **4a** ($R_2 =$ Ph, Me).

In conclusion, we have prepared novel Si-bridged bithiophene derivatives and found that they have low-lying LUMO and may be used as the electron-transport for EL devices. However, the electron-transporting properties of the vapor deposited films of **1b** and **2b** estimated on the basis of the EL device performance were inferior to those of **3a** ($R = p$-Tol), **4a** ($R_2 =$ Ph, Me), and Alq. This is in contrast to that the LUMOs of **1b** and **2b** were predicted to lie at similar and lower energies, respectively, as compared with those of **3a** and **4a**, by the UV and CV data as well as by the MO calculations on the model compounds. However, factors other than just the LUMO energy levels of the Si-bridged bithiophenes, including packing structures in the vapor deposited layer, seem to be also important for the electron-transport in the solid state.

3. Experimental

3.1. General

All reactions were carried out under an inert atmosphere. NMR spectra were recorded on JEOL Model JNM-EX 270 and JEOL Model JNM-LA 400 spectrometers. Mass spectra were measured with a Hitachi M80B spectrometer. UV spectra were measured on a Hitachi U-3210 spectrophotometer.

3.2. Materials

THF and ether were dried over Na–K alloy and distilled just before use. Acetonitrile was distilled from P_2O_5 and stored in dark under an argon atmosphere at 4 °C before use.

3.3. Preparation of *1a–c* and *2a*, *b*

To a solution of 3,3′-dilithio-5,5′-bis(trimethylsilyl)-2,2′-bithiophene, prepared from 3.74 g (8.00 mmol) of 3,3′-dibromo-5,5′-bis(trimethylsilyl)-2,2′-bithiophene and 10.0 ml (16.0 mmol) of a 1.6 M solution of *n*-butyllithium–hexane in 20 ml of ether, was added 1.71 g (4.00 mmol) of *p*-bis(dichlorophenylsilyl)benzene at − 80 °C. The mixture was warmed to room temperature (r.t.) and 30 ml of THF was added to the mixture, then the mixture was heated to reflex for 20 h. After hydrolysis of the mixture, the organic products were separated, and the aq. layer was extracted with hexane. The organic layer and the extracts were combined and dried over anhydrous $MgSO_4$. After evaporation of the solvents, the residue was chromatographed on a silica gel column with hexane as eluent to give crude solids. The crude solids were recrystallized from EtOH to give 1.2 g (31% yield) of **1a** as the colorless crystals: m.p. 135–137 °C; MS m/z 902 [M^+]; ^{1}H-NMR (δ in $CDCl_3$) 0.44 (s, 36H, Me_3Si), 7.40 (s, 4H, thiophene),

Table 2
Performance of EL devices[a] having a Si-bridged bithiophene layer as the electron-transport and the reference device[b]

Si-bridged bithiophene	Threshold voltage[c] of 100 mA cm^{-2} (V)	Threshold voltage[d] of 1000 cd m^{-2} (V)	Maximal current density[e] (mA cm^{-2})	Maximal luminance[e] (cd m^{-2})
1b	15.0	13.0	350 (18.0)	6300 (16.0)
2b	13.3	12.5	400 (15.0)	8500 (17.0)
3a ($R = p$-Tol)	11.2	11.0	600 (13.5)	8000 (13.0)
4a ($R_2 =$ Ph, Me)	12.5	12.4	500 (15.0)	6000 (14.5)
Reference device	12.1	11.5	550 (14.5)	10 000 (14.0)

[a] ITO/TPD (40 nm)/Alq (50 nm)/Si-bridged bithiophene (10–20 nm)/Mg–Ag.

[b] ITO/TPD (40 nm)/Alq (50 nm)/Mg–Ag.

[c] Applied voltage resulting in the current density of 100 mA cm^{-2}.

[d] Applied voltage resulting in the luminance of 1000 cd m^{-1}.

[e] Numbers in parentheses indicate the applied voltage (V) resulting in the maximum current density and luminance.

7.42–7.51 (m, 6H, Ph), 7.76 (*d*, 4H, $J = 1.7$ Hz, *o*-Ph) 7.78 (s, 4H, phenylene); ^{13}C-NMR (δ in $CDCl_3$) 0.1 (Me_3Si), 128.1, 130.3, 131.8, 134.6, 134.9, 135.4 (Ph), 136.4 (C3, C5), 141.4 (C2, C6), 142.3 (C7a, b), 155.6 (C3a, C4a); ^{29}Si-NMR (δ in $CDCl_3$) -6.7 ($SiMe_3$), -22.1 (silole Si). Anal. Calc. for $C_{46}H_{54}S_4Si_6$: C, 61.14; H, 6.02. Found: C, 60.84; H, 6.04%.

Compounds **1b**, **c** and **2a**, **b** were prepared in a similar fashion to above. Data for **1b** (after recrystallization from ethanol): 47% yield; m.p. 144–145 °C; MS *m*/*z* 862 [M^+]; ^{1}H-NMR (δ in $CDCl_3$) 0.37 (s, 36H, Me_3Si), 0.87–0.90 (br t, 6H, $J = 7.21$ Hz, *n*-Bu), 1.19–1.23 (m, 4H, *n*-Bu), 1.33–1.43 (m, 4H, *n*-Bu), 1.46–1.52 (m, 4H, *n*-Bu), 7.22 (s, 4H, thiophene), 7.62 (s, 4H, phenylene); ^{13}C-NMR (δ in $CDCl_3$) 0.1 (Me_3Si), 11.9, 13.6, 26.3 (*n*-Bu, One carbon signal is overlapping) 135.3, 135.3 (phenylene), 136.5 (C3, C5), 141.7 (C2, C6), 142.3 (C7a, b), 155.1 (C3a, C4a); ^{29}Si-NMR (δ in $CDCl_3$) -6.9 ($SiMe_3$), -15.0 (silole Si). Anal. Calc. for $C_{42}H_{62}S_4Si_6$: C, 58.40; H, 7.24. Found: C, 58.61; H, 7.50%. Data for **1c** (after recrystallization from EtOH): 65% yield; m.p. 128–129 °C; MS *m*/*z* 874 [M^+]; ^{1}H-NMR (δ in $CDCl_3$) -0.18 (s, 18H, Me_3SiCH_2), 0.07 (s, 4H, ethylene), 0.31 (s, 36H, Me_3Si-thiophene), 0.84 (s, 4H, CH_2SiMe_3), 7.10 (s, 4H, thiophene); ^{13}C-NMR (δ in $CDCl_3$) -1.7 (ethylene) 0.1 (Me_3Si–thiophene), 0.7 ($\mathit{CH_2}SiMe_3$), 7.5 ($\mathit{Me_3}SiCH_2$), 136.8 (C3, C5), 141.0 (C2, C6), 144.4 (C7a, b), 154.3 (C3a, C4a); ^{29}Si-NMR (δ in $CDCl_3$) 1.0 (Me_3SiCH_2), -7.1 (Me_3Si-thiophene), -7.7 (silole Si). Anal. Calc. for $C_{38}H_{66}S_4Si_8$: C, 52.11; H, 7.60. Found: C, 51.86; H, 7.55%. Data for **2a** (after recrystallization from hexane): 5% yield; m.p. 269–270 °C; MS *m*/*z* 702 [M^+]; ^{1}H-NMR (δ in $CDCl_3$) 0.32 (s, 36H, Me_3Si), 0.68 (s, 6H, Me), 7.28 (s, 4H, thiophene); ^{13}C-NMR (δ in $CDCl_3$) -4.2 (Me) 0.0 (Me_3Si), 131.5, 139.5, 139.9, 151.3 (thiophene); ^{29}Si-NMR (δ in $CDCl_3$) -6.7 ($SiMe_3$), -49.8 (Si–Si). Anal. Calc. for $C_{30}H_{46}S_4Si_6$: C, 51.22; H, 6.59. Found: C, 51.00; H, 6.70%. Data for **2b** (after recrystallization from hexane): 10% yield; m.p. 267–269 °C; MS *m*/*z* 786 [M^+]; ^{1}H-NMR (δ in $CDCl_3$) 0.38 (s, 36H, Me_3Si), 0.35–1.22 (m, 18H, *sec*-Bu), 7.44 (s, 4H, thiophene); ^{13}C-NMR (δ in $CDCl_3$) 0.0 (Me_3Si), 13.0, 13.4, 23.3 25.0 (*sec*-Bu), 131.3, 139.1, 139.9, 152.0 (thiophene); ^{29}Si-NMR (δ in $CDCl_3$) -6.8 ($SiMe_3$), -36.9 (Si–Si). Anal. Calc. for $C_{36}H_{58}S_4Si_6$: C, 54.89; H, 7.42. Found: C, 55.02; H, 7.61%.

3.4. CV measurements

CV measurements were carried out using a three-electrode system in acetonitrile solutions containing 100 mM of lithium perchlorate as the supporting electrolyte and 4 mM of the substrate. A glassy carbon electrode, platinum plate, and SCE were used as the working, counter and reference electrodes, respectively. The current–voltage curves were recorded at r.t. on a Hokuto Denko HAB-151 potentiostat–galvanostat.

3.5. Preparation of EL devices

Each layer of the EL devices was prepared by vacuum deposition at 1×10^{-5} torr in the order of TPD, Alq, and Si-bridged bithiophene, on ITO coated on a glass substrate with a sheet resistance of 15 Ω cm^{-1} (Asahi Glass Company). Finally a layer of magnesium–silver alloy with an atomic ratio of 10:1 was vacuum deposited as the top electrode. The thickness of each layer of the EL devices was measured with a Sloan Dektak 3030 surface profiler. The emitting area was 0.5×0.5 cm^2. Luminance was measured with a Topcon luminance meter BM-7 at r.t.

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[8] Crystal data for **2b**: $C_{36}H_{58}S_4Si_6$, MW = 787.61, space group $C2/m$ (no. 12) with $a = 9.41(2)$, $b = 27.21(2)$, $c = 9.64(2)$ Å, $\beta = 109.7(2)$ (°), $V = 2323(9)$ Å^3, $Z = 2$, $D_{calc} = 1.126$ g cm^{-3}, $F(000) = 844.00$, $\mu(Mo{-}K_\alpha) = 3.82$ mm^{-1}. Data were collected on a Rigaku AFC7R diffractometer by the $2\theta{-}\omega$ method, using a $0.7 \times 0.7 \times 0.1$ mm sized crystal. 1320 unique reflections; with $I > 3\sigma(I)$ were used in refinement. All calculations were performed using the TEXSAN crystallographic software package (Molecular structure corporation, 1985 and 1992) with the residuals of $R = 15.0\%$, $R_w = 17.4\%$, ref/par = 11.09.

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